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Pharmaceuticals and Other Organic Chemicals in Selected North-Central and Northwestern Arkansas Streams

Brian E. Haggard,* Joel M. Galloway, W. Reed Green, and Michael T. Meyer

ABSTRACT

Recently, our attention has focused on the low level detection of many antibiotics, pharmaceuticals, and other organic chemicals in water resources. The limited studies available suggest that urban or rural streams receiving wastewater effluent are more susceptible to contamination. The purpose of this study was to evaluate the occurrence of antibiotics, pharmaceuticals, and other organic chemicals at 18 sites on seven selected streams in Arkansas, USA, during March, April, and August 2004. Water samples were collected upstream and downstream from the influence of effluent discharges in northwestern Arkansas and at one site on a relatively undeveloped stream in north-central Arkansas. At least one antibiotic, pharmaceutical, or other organic chemical was detected at all sites, except at Spavinaw Creek near Mayesville, Arkansas. The greatest number of detections was observed at Mud Creek downstream from an effluent discharge, including 31 pharmaceuticals and other organic chemicals. The detection of these chemicals occurred in higher frequency at sites downstream from effluent discharges compared to those sites upstream from effluent discharges; total chemical concentration was also greater downstream. Wastewater effluent discharge increased the concentrations of detergent metabolites, fire retardants, fragrances and flavors, and steroids in these streams. Antibiotics and associated degradation products were only found at two streams downstream from effluent discharges. Overall, 42 of the 108 chemicals targeted in this study were found in water samples from at least one site, and the most frequently detected organic chemicals included caffeine, phenol, *para*-cresol, and acetyl hexamethyl tetrahydro naphthalene (AHTN).

A WIDE VARIETY OF CHEMICALS can enter streams through municipal wastewater treatment plant (WWTP) effluent discharges, including prescription and nonprescription drugs, hormones, antimicrobial agents, pesticides, disinfectants, and fragrances. Although many of these synthetic organic chemicals were developed and are used for beneficial purposes, the occurrence of these chemicals in surface and ground water resources has prompted the recognition of potential ecological and human health concerns. For example, the antimicrobial agent triclosan that is often found in WWTP effluents (Lindstrom et al., 2002) may affect algal growth and community structure (Wilson et al., 2003; White et al., 2005) and is suspected of increasing antibiotic resistance in multiple bacterial lineages (McMurry et al., 1998). Reiss et al. (2002) concluded that the potential exists for triclosan to affect aquatic organisms downstream from effluent discharges, especially during low flow periods when dilution is minimal. In reality, little is known about the potential adverse effects from chronic environmental exposure to these individual chemicals and chemical mixtures at very low doses on aquatic biota, other terrestrial animals, and also humans.

Just recently, analytical methods have been developed that are capable of detecting these chemicals at very low levels found in the environment (Hirsch et al., 1998; Lindsey et al., 2001; Cahill et al., 2004), particularly in streams and ground waters (e.g., see Kolpin et al., 2002; Barnes et al., 2004; Derksen et al., 2004). The limited studies available indicate that urban or rural streams receiving effluent discharges from municipal WWTPs or animal feeding operations are at greatest risk of contamination from these chemicals. Although limited data are available, it appears that the occurrence of these organic wastewater compounds (OWCs) and other organic chemicals was widely prevalent in surface waters and that an increasing number of chemicals are being detected (Ternes, 1998; Kolpin et al., 2002; Derksen et al., 2004; Sprague and Battaglin, 2005). The purpose of this study was to provide a reconnaissance of the occurrence of antibiotics, pharmaceuticals, and other organic chemicals of emerging concern in selected streams in northwestern and north-central Arkansas. The importance of this survey study was to provide an inventory of pharmaceuticals and other organic chemicals that may be found in these streams so that more detailed studies can be conducted on the transport and fate of these chemicals in aquatic environments.

MATERIALS AND METHODS

Water samples were collected in March, April, and August 2004 from 18 sites on eight different streams in northwestern and north-central Arkansas (Fig. 1, Table 1). The sampling site (Site 3) and stream selected in north-central Arkansas was North Sylamore Creek near Fifty-Six, Arkansas, representing a sampling site that drains a relatively undeveloped, mostly forested catchment. North Sylamore Creek is part of the U.S. Geological Survey Hydrologic Benchmark Network which includes sites across the nation where long-term measurements of stream discharge and water-quality data are collected. The other sampling sites and streams in northwestern Arkansas were targeted because these streams receive

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Abbreviations: AHTN, acetyl hexamethyl tetrahydro naphthalene; OWC, organic wastewater compound; WWTP, wastewater treatment plant.

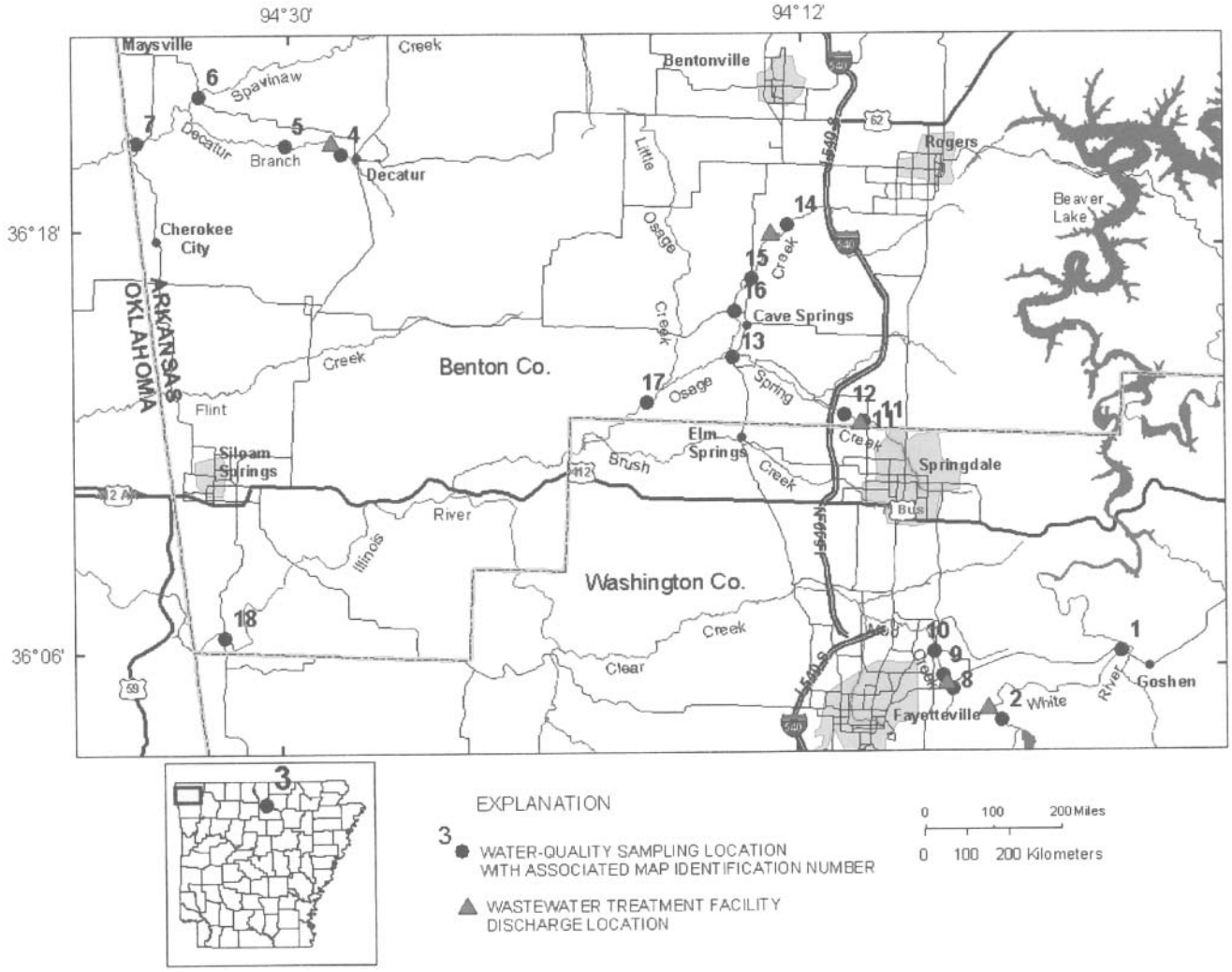

Fig. 1. Study area with selected water-quality sampling locations at streams in north-central and northwestern Arkansas, USA, 2004.

WWTP effluent discharge from the cities of Decatur, Fayetteville, Springdale, and Rogers, Arkansas. Sampling sites were selected upstream and downstream from the effluent discharges on Decatur Branch (locally named Columbia Hollow) and Spavinaw Creek (Decatur WWTP), Mud Creek and the White River (Fayetteville WWTP), Spring Creek (Springdale WWTP), and Osage Creek (Rogers WWTP). An additional site was selected at Osage Creek (Site 17) downstream from the Rogers and Springdale WWTP effluent discharge and at the Illinois River (Site 18) over 45 river km downstream from the Fayetteville, Rogers, and Springdale WWTP effluent discharges. These sampling sites and streams in northwestern Arkansas drain catchments with varying proportions of pasture, forest, and urban–suburban areas.

Water samples were collected and processed using protocols described in Wilde et al. (1998a, 1998b, 1998c, 1999a, 1999b). Water samples were collected from a single vertical point in the stream due to well-mixed conditions, low velocities, and relatively small cross-sectional areas at the streams. Water samples were filtered on-site through a 0.7-μm-pore-size, oven-baked glass fiber filter and then shipped to the respective laboratories in amber glass bottles, chilled to 4°C. To minimize contamination of samples, use of personal care products, caffeinated products, pharmaceuticals, and tobacco were minimized during sample collection and processing. Water sampling technicians also wore gloves to further minimize the risk of contamination during sample processing. Field parameters (water temperature, pH, dissolved oxygen, and specific conductance) were also measured at each site, following the protocols described in Wilde and Radke (1998). Discharge measurements were made at each site using an acoustic Doppler current profiler and methods described in Rantz et al. (1982). All 18 sites were sampled in March and April 2004, and one field duplicate and one field blank sample were collected during this sampling period for quality assurance and quality control (QA–QC). A second set of routine samples was collected at three sites on Mud Creek (Sites 8, 9, and 10) in August 2004, including one field duplicate and one field blank sample. Physicochemical data are reported in Table 2; however, this data is not specifically discussed in this manuscript.

Water samples were analyzed for OWCs and other organic chemicals by the U.S. Geological Survey National Water Quality Laboratory in Lakewood, Colorado; specific details of these analytical procedures may be obtained in Zaugg et al. (2002). Water samples were extracted for OWCs through disposable solid-phase extraction (SPE) cartridges containing polystyrene–divinylbenzene resin within 1 wk of water sample collection; cartridges were dried with nitrogen gas and then sorbed chemicals were eluted with dichloromethane–diethyl ether. The OWC and other organic concentrations were mea-

Table 1. Water-quality monitoring site characteristics at select streams in north-central and northwestern Arkansas sampled in March, April, and August 2004 and site location relative to municipal wastewater treatment plant effluent discharges from the City of Fayetteville (COF), City of Decatur (COD), City of Rogers (COR), and City of Springdale (COS).

Site	USGS site ID	USGS site name	Relative to WWTP†	Number of detections	
				OWCs‡	Antibiotics
1	07048600	White River near Fayetteville	upstream	2	0
2	07048700	White River near Goshen	downstream from COF discharge	2	0
3	07060710	North Sylamore Creek near Fifty-Six	benchmark	2	0
4	36201609-4280500	Decatur Branch at Decatur	upstream	5	0
5	36203009-4300400	Decatur Branch near Mayesville	downstream from COD discharge	6	0
6	07191160	Spavinaw Creek near Mayesville	upstream	0	0
7	07191179	Spavinaw Creek near Cherokee City	downstream from COD discharge	3	0
8	36051609-4063400	Mud Creek south of Hwy 45 at Fayetteville	upstream	3, 2§	0, 0§
9	36053809-4065500	Mud Creek at Township Rd at Fayetteville	downstream from COF discharge	17, 23§	4, 8§
10	36061909-4071200	Mud Creek at Old Wire Rd at Fayetteville	downstream from COF discharge	21, 22§	4, 8§
11	36124809-4094200	Spring Creek at Silent Grove Rd near Springdale	upstream	7	0
12	36130109-4102400	Spring Creek at North 40th St near Springdale	downstream from COS discharge	20	2
13	36143809-4141900	Spring Creek at Hwy 112 near Cave Springs	downstream from COS discharge	18	0
14	36182309-4122700	Osage Creek near CR 51 near Rogers	upstream	1	0
15	07194880	Osage Creek near Cave Springs	downstream from COR discharge	21	0
16	36155609-4141600	Osage Creek at Hwy 264 at Cave Springs	downstream from COR discharge	13	0
17	07195000	Osage Creek near Elm Springs	downstream from COR and COS discharge	14	0
18	07195430	Illinois River south of Siloam Springs	downstream from COF, COR, and COS discharge	4	0

† Wastewater treatment plant.
‡ Organic wastewater compound.
§ Number of detections in the water samples collected in August 2004; OWCs denote pharmaceuticals excluding antibiotics and other organic chemicals measured in water samples at the USGS National Water Quality Laboratory.

sured using capillary-column gas chromatography (GC) and mass spectrometry (MS) (see Zaugg et al., 2002). These methods were developed to measure 63 chemical concentrations because these chemicals may enter the environment through wastewater effluent and may be used in high quantities (Kolpin et al., 2002). These OWCs and other organic chemicals may be separated into these categories: antioxidants, detergent metabolites, disinfectants and disinfection by-products (hereafter, disinfectants), fire retardants, fragrances and flavors, insect repellents and pesticides, nonprescription drugs, polyaromatic hydrocarbons, plasticizers, solvents, and steroids. In this paper, the steroid compounds measured in water samples do not refer to steroid hormones, which have been shown to have adverse effects on aquatic organisms (Colborn et al., 1993). Several chemicals measured in the lab analyses are not exclusively found in effluent discharges from WWTPs.

Water samples were analyzed for antibiotics and antibiotic residuals at the U.S. Geological Survey Organic Geochemistry Research Laboratory in Lawrence, Kansas. Water samples were extracted within 1 wk of water sample collection and analyzed for five classes of antibiotics (beta lactams, macrolides, quinolones, sulfonamides, and tetracyclines). Three online solid phase extraction methods with different mobile phase solutions were used to separate antibiotics, and liquid chromatography (LC) and MS or LC–MS–MS were used to determine antibiotic concentrations in the sample extracts (see Hirsch et al., 1998; Lindsey et al., 2001). Specific details on these analytical procedures may found at http://www-ks.cr.usgs.gov/Kansas/studies/reslab/method.html (verified 13 Mar. 2006).

All data reported within this paper are available at http://waterdata.usgs.gov/ar/nwis/qw/ (verified 13 Mar. 2006). Total

Table 2. Physicochemical measurements associated with water samples collected at select streams in north-central and northwestern Arkansas streams, 2004.

Site	USGS site name	Q†	Dissolved oxygen	pH	Specific conductance	Temperature
		L s^{-1}	mg L^{-1}		µS cm^{-1}	°C
1	White River near Fayetteville	13640	9.2	7.4	74	14
2	White River near Goshen	13527	9.6	7.6	79	14
3	North Sylamore Creek near Fifty-Six	170	9.7	7.9	279	18
4	Decatur Branch at Decatur	59	9.5	7.5	232	12
5	Decatur Branch near Mayesville	133	9.9	7.6	419	13
6	Spavinaw Creek near Mayesville	2179	10.0	7.5	282	13
7	Spavinaw Creek near Cherokee City	2321	12.3	8.2	290	13
8	Mud Creek south of Hwy 45 at Fayetteville	5, <3‡	8.6, 6.1‡	8.0, 7.6‡	269, 252‡	14, 20‡
9	Mud Creek at Township Rd at Fayetteville	175, 174‡	9.9, 7.7‡	8.1, 7.8‡	665, 568‡	15, 23‡
10	Mud Creek at Old Wire Rd at Fayetteville	224, 163‡	9.8, 7.8‡	8.3, 8.0‡	611, 581‡	15, 23‡
11	Spring Creek at Silent Grove Rd near Springdale	212	9.5	7.3	340	16
12	Spring Creek at North 40th St near Springdale	764	9.7	7.6	673	17
13	Spring Creek at Hwy 112 near Cave Springs	1104	10.6	8.6	570	16
14	Osage Creek near CR 51 near Rogers	481	9.2	7.3	295	12
15	Osage Creek near Cave Springs	1104	10.9	7.8	388	14
16	Osage Creek at Hwy 264 at Cave Springs	1019	11.0	8.0	380	15
17	Osage Creek near Elm Springs	3538	10.9	8.3	381	15
18	Illinois River south of Siloam Springs	9792	11.6	8.1	315	16

† Instantaneous discharge measured at time of water sample collection.
‡ Data collected during the second round of water sample collection in August 2004.

concentration presented in Results and Discussion was the sum of the concentration of all constituents within a chemical category across all sampling sites or within an individual site.

RESULTS AND DISCUSSION

Pharmaceuticals and Other Organic Chemicals

One or more pharmaceuticals and other organic chemicals were found in water samples collected at all of the sampling sites in this study (Table 1), except at Spavinaw Creek near Mayesville, Arkansas (Site 6). The relatively high frequency of detection of many contaminants was likely influenced by sampling site selection; this study intentionally chose several sites downstream from effluent discharges in northwestern Arkansas. Northwestern Arkansas also has a high density of poultry production and processing facilities, and land application of poultry manure as an organic fertilizer is typical. However, these water samples were collected during base flow conditions where detection of potential diffuse sources of organic contaminants was likely minimal. The only site where these chemicals were not detected in measurable concentrations drains an agricultural catchment with a high density of poultry farms. However, the chemicals targeted in this investigation were more specific to those associated with human activities. Detergent metabolites, disinfectants, fire retardants, fragrances and flavors, insect repellents and pesticides, nonprescription drugs, and plasticizers were detected in measurable concentration in more than 40% of the collected water samples (Fig. 2).

The number of pharmaceuticals and other organic chemicals detected was variable, from 1 to 23 at the selected study sites. Mixtures of these chemicals were widely prevalent across these streams because more than one chemical was detected at 16 of the 18 sampling sites; 7 sampling sites had greater than 12 chemicals detected. The mean number of detections was significantly greater (paired t test, $P = 0.035$) at the first site downstream (approximately 14 detections) from the effluent discharges compared to the upstream sites (approximately 4 detections) in our study area (Fig. 3); the difference between total concentration upstream and downstream

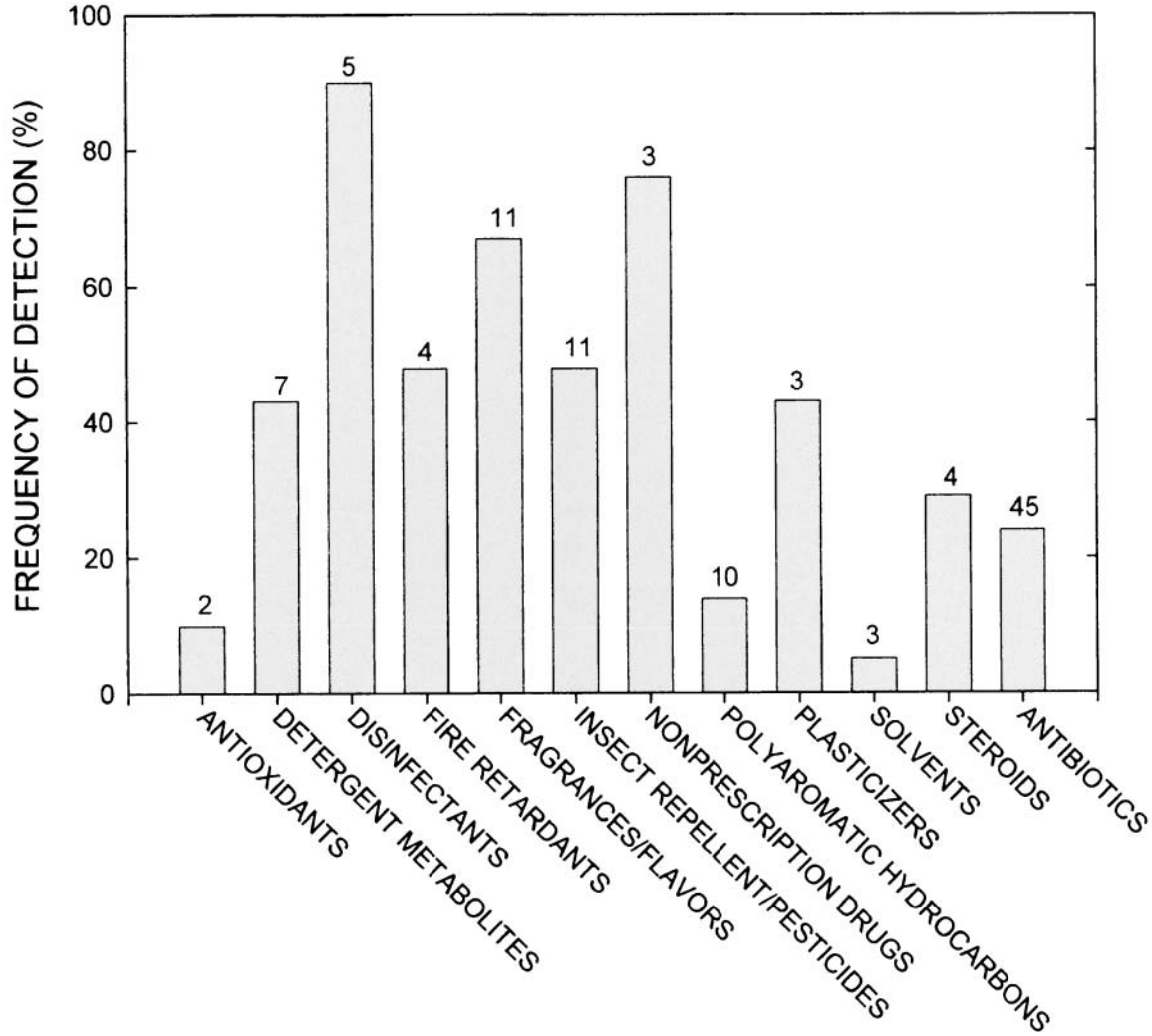

Fig. 2. Frequency of detection of the various pharmaceutical and other organic chemical categories in the collected water samples from selected streams in north-central and northwestern Arkansas, 2004. Numbers above vertical bars denote the number of individual constituents within a given category.

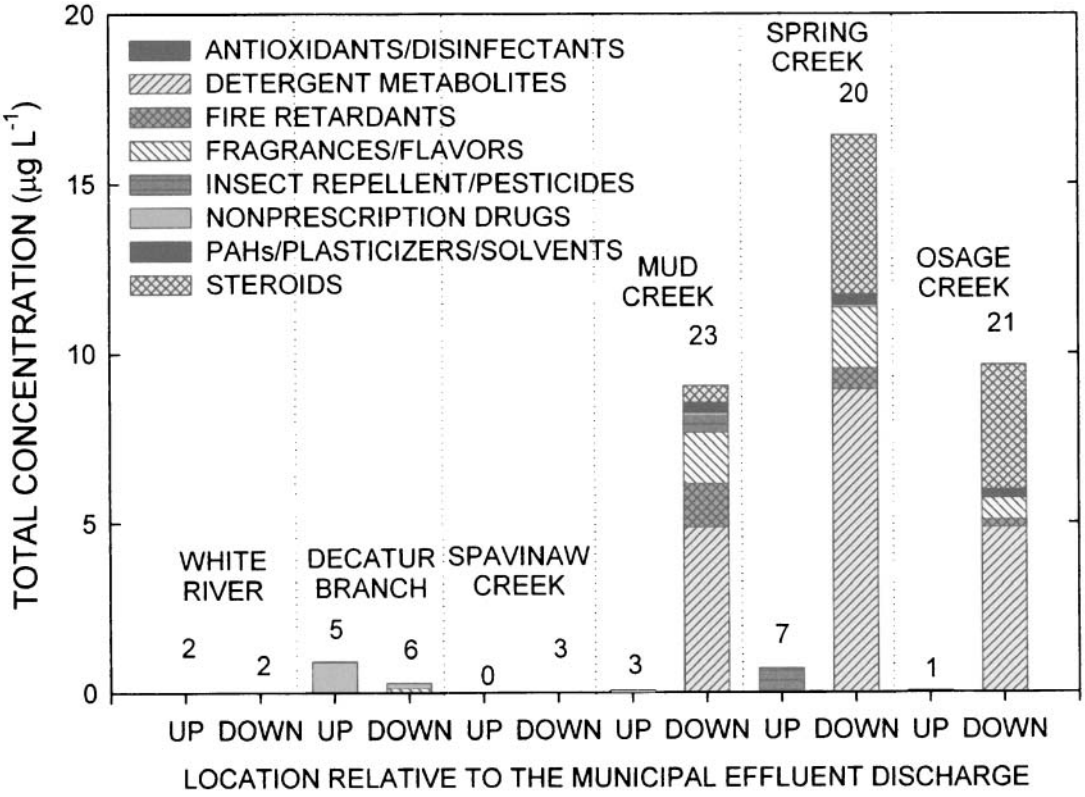

Fig. 3. Total concentrations of the various pharmaceutical and other organic chemical categories in water samples collected at sites upstream and downstream of effluent discharges on the White River, Decatur Branch, Spavinaw Creek, Mud Creek, Spring Creek, and Osage Creek, 2004. The data from Mud Creek represent the average total concentration of various organic wastewater compound (OWC) categories from the water samples collected in March and August 2004; numbers above the vertical bars represent the number of chemicals detected in the collected water samples at each site.

was only marginally significant (ln-transformed data, paired *t* test, $P = 0.094$). The number of detections was greatest at sites downstream from effluent discharges where WWTPs more than doubled stream discharge (Tables 1 and 2). The number of detections and concentrations of chemicals detected generally decreased with increased distance downstream from the WWTP effluent discharges. Several previous investigations have shown these chemicals are in measurable concentrations and prevalent downstream from effluent discharges (e.g., see Ternes, 1998; Daughton and Ternes, 1999; Sprague and Battaglin, 2005). In this study, several categories of these chemicals were more prevalent downstream from effluent discharges, including detergent metabolites, fragrances and flavors, and steroids (Fig. 3). However, nonprescription drugs and disinfectants were found in the greatest frequency in the water samples collected in this study. Detergent metabolites, disinfectants, insect repellent, nonprescription drugs, and steroids are the chemicals categories usually detected in greatest frequency in similar USGS investigations of streams and ground waters across the United States (Boyd and Furlong, 2002; Kolpin et al., 2002; Sprague and Battaglin, 2005).

Although the number of detections was greater downstream from WWTPs, several pharmaceuticals and other organic chemicals were widely detected at sites not influenced by effluent discharge indicating the presence of natural sources (e.g., decomposing organic matter) or other anthropogenic sources unrelated to WWTPs (e.g., wood preservatives and pesticide adjuvants). For example, caffeine, phenol, and acetyl hexamethyl tetrahydro naphthalene (AHTN) were even found at North Sylamore Creek near Fifty-Six, Arkansas (Site 3); this site was selected because it drains a relatively undeveloped catchment. Caffeine and phenol were found at five of seven sites that are not downstream from an effluent discharge, whereas *para*-cresol was found at three sites; these chemicals represent nonprescription drugs and disinfectants, which were found with the greatest frequency in this study.

Overall, 34 of the 63 targeted pharmaceuticals and other OWCs were detected at least once during this study (Table 3), and measured concentrations were generally low (maximum detectable concentration was generally <1 μg L^{-1}). Many of the reported chemical concentrations were estimated because the concentrations were less than the reporting limit (RL) for a given chemical. However, a few constituents had detectable concentrations of >1 μg L^{-1}, including 3-β-coprostanol, *para*-nonylphenol (total), AHTN, β-sigmaterol, cholesterol, diethoxy-nonylphenol (total, NPEO2), and monoethoxy-octylphenol (OPEO1).

Total concentrations of the various chemical categories exceeded 1 μg L^{-1}, except polycyclic aromatic hydrocarbons (PAHs) and solvents (Fig. 4); total con-

Table 3. Summary of analytical results for several pharmaceutical and other organic chemicals in the water samples collected from selected streams in north-central and northwestern Arkansas, March, April, and August 2004.

Organic wastewater compound (OWC)	RL†	Frequency‡	Reported concentration in water samples			Primary use category§
			Minimum	Median	Maximum	
	μg L^{-1}	%	μg L^{-1}			
3-*tert*-Butyl-4-hydroxyanisole (BHA)	5.0	0	–	–	–	antioxidant
5-Methyl-1*H*-benzotriazole¶	2.0	10	E 0.620#	–	E 0.760	antioxidant
4-Cumylphenol	1.0	0	–	–	–	detergent metabolite
4-*n*-Octylphenol	1.0	0	–	–	–	detergent metabolite
para-Nonylphenol (total)¶	0.5	29	0.510	0.765	1.200	detergent metabolite
4-*tert*-Octylphenol¶	0.5	10	E 0.140	–	E 0.180	detergent metabolite
Nonylphenol, diethoxy- (total, NPEO2)¶	5.0	33	E 2.60	E 3.60	7.40	detergent metabolite
Octylphenol, diethoxy- (OPEO2)¶	1.0	29	E 0.130	E 0.275	E 0.680	detergent metabolite
Octylphenol, monoethoxy- (OPEO1)¶	1.0	14	E 0.460	E 0.900	E 1.1	detergent metabolite
1,4-Dichlorobenzene¶	0.5	14	E 0.027	E 0.081	E 0.098	disinfectant
Bromoform¶	0.5	24	E 0.012	E 0.018	E 0.041	disinfectant
para-Cresol¶	1.0	67	E 0.031	E 0.053	E 0.150	disinfectant
Phenol¶	0.5	81	E 0.110	E 0.260	0.990	disinfectant
Triclosan¶	1.0	24	E 0.062	E 0.130	E 0.250	disinfectant
Tri(2-butoxyethyl) phosphate¶	0.5	0	–	–	–	fire retardant
Tri(2-chloroethyl) phosphate¶	0.5	48	E 0.048	E 0.195	0.700	fire retardant
Tri(dichloroisopropyl) phosphate¶	0.5	43	E 0.100	E 0.200	E 0.400	fire retardant
Tributyl phosphate¶	0.5	43	E 0.031	E 0.100	0.560	fire retardant
3-Methyl-1*H*-indole¶	1.0	10	E 0.044	–	E 0.091	fragrances, flavors
Acetophenone	0.5	0	–	–	–	fragrances, flavors
Acetyl hexamethyl tetrahydro naphthalene (AHTN)¶	0.5	62	E 0.008	E 0.480	1.4	fragrances, flavors
Benzophenone¶	0.5	43	E 0.031	E 0.120	E 0.160	fragrances, flavors
Camphor	0.5	0	–	–	–	fragrances, flavors
d-Limonene¶	0.5	5	E 0.029	–	–	fragrances, flavors
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)¶	0.5	48	E 0.026	E 0.117	E 0.24	fragrances, flavors
Indole¶	0.5	10	E 0.024	–	E 0.026	fragrances, flavors
Isoborneol	0.5	0	–	–	–	fragrances, flavors
Isoquinoline	0.5	0	–	–	–	fragrances, flavors
Menthol	0.5	0	–	–	–	fragrances, flavors
N,N-diethyl-*meta*-toluamide (DEET)¶	0.5	43	E 0.018	E 0.028	E 0.083	insect repellent
Bromacil¶	0.5	14	0.650	0.750	0.790	pesticides
Carbaryl¶	1.0	10	E 0.070	–	E 0.076	pesticides
Carbazole	0.5	0	–	–	–	pesticides
Chlorpyrifos	0.5	0	–	–	–	pesticides
Diazinon¶	0.5	5	E 0.034	–	–	pesticides
Dichlorvos	1.0	0	–	–	–	pesticides
Metalaxyl	0.5	0	–	–	–	pesticides
Metolachlor	0.5	0	–	–	–	pesticides
Pentachlorophenol	2.0	0	–	–	–	pesticides
Prometon	0.5	0	–	–	–	pesticides
Caffeine¶	0.5	76	E 0.032	E 0.045	0.880	nonprescription drug
Cotinine¶	0.5	14	E 0.036	E 0.048	E 0.052	nonprescription drug
Methyl salicylate	0.5	0	–	–	–	nonprescription drug
1-Methylnaphthalene	0.5	0	–	–	–	PAHs††
2,6-Dimethylnaphthalene	0.5	0	–	–	–	PAHs
2-Methylnaphthalene	0.5	0	–	–	–	PAHs
Anthraquinone	0.5	0	–	–	–	PAHs
Anthracene	0.5	0	–	–	–	PAHs
Benzo[*a*]pyrene	0.5	0	–	–	–	PAHs
Fluoranthene	0.5	0	–	–	–	PAHs
Naphthalene¶	0.5	14	E 0.016	E 0.018	E 0.020	PAHs
Phenanthrene	0.5	0	–	–	–	PAHs
Pyrene	0.5	0	–	–	–	PAHs
Bisphenol A	1.0	0	–	–	–	plasticizers
Triethyl citrate (ethyl citrate)¶	0.5	43	E 0.140	E 0.220	E 0.270	plasticizers
Triphenyl phosphate¶	0.5	43	E 0.009	E 0.034	E 0.063	plasticizers
Isophorone	0.5	0	–	–	–	solvents
Isopropylbenzene (cumene)	0.5	0	–	–	–	solvents
Tetrachloroethylene¶	0.5	5	E 0.012	–	–	solvents
3-*beta*-Coprostanol¶	2.0	29	E 0.240	E 0.775	E 1.50	steroids
beta-Sitosterol¶	2.0	5	E 0.970	–	–	steroids
beta-Stigmastanol¶	2.0	14	E 0.870	E 0.950	E 1.60	steroids
Cholesterol¶	2.0	29	E 0.540	E 0.960	E 1.60	steroids

† Method reporting limiting from the U.S. Geological Survey National Water-Quality Laboratory.
‡ Frequency of constituent detection in percent for 21 water samples collected in March, April, and August 2004 (Mud Creek sites were sampled twice).
§ Information adapted from Zaugg et al. (2002) and Sprague and Battaglin (2005).
¶ Detected in measurable concentrations by analytical methods used in this study.
# The term "E" defines concentrations that were estimated at or below the reporting limit of the method used.
†† Polycyclic aromatic hydrocarbons.

centration refers to the sum of individual concentrations across all water samples within an organic chemical category. The greatest total concentrations were observed with detergent metabolites (38.6 μg L^{-1}) and steroids (14.5 μg L^{-1}); however, detergent metabolites and steroids were found in less than half of the collected water

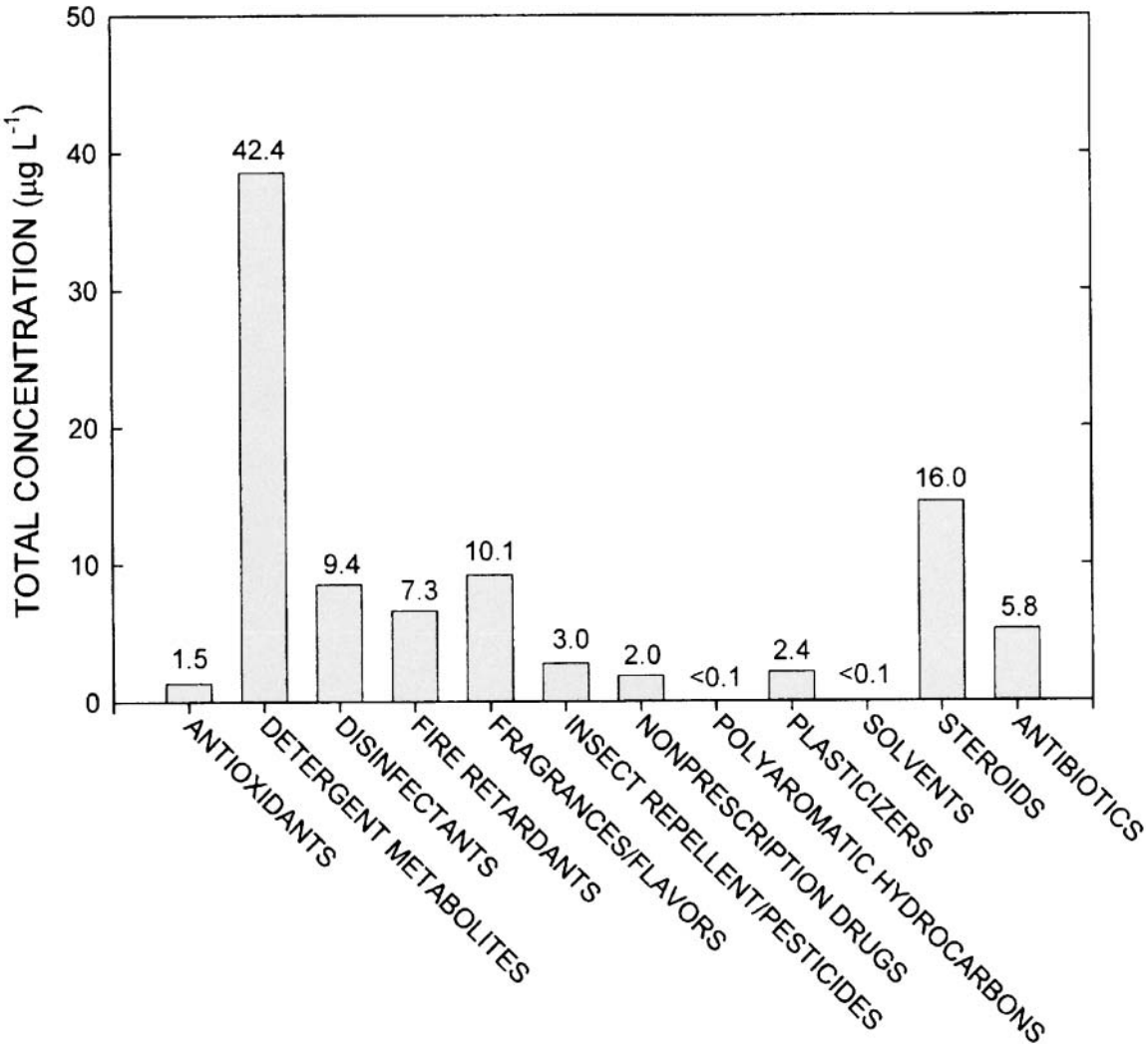

Fig. 4. Total concentrations of the various pharmaceutical and other organic chemical categories in the collected water samples from selected streams in north-central and northwestern Arkansas, 2004. Numbers above vertical bars denote the percent of the total organic wastewater compound (OWC) measured concentration.

samples. Individual pharmaceuticals and other OWCs detected in the greatest frequency (>50% of water samples) included AHTN, caffeine, *para*-cresol, and phenol.

None of the individual compounds targeted in this study exceeded drinking water guidelines, health advisories, or aquatic life criteria (as summarized in Kolpin et al., 2002), although there may be unknown consequences related to long-term low level exposure to these chemicals, associated degradation products, and mixtures in the environment (Daughton and Ternes, 1999; Boxall et al., 2004). This paper demonstrates that many of these chemicals occur in mixtures at low concentrations in streams in northwestern Arkansas, especially in those streams influenced by municipal WWTP effluent discharge.

Antibiotics

Kolpin et al. (2002) detected antibiotics and associated degradation products in about half of the 139 streams targeted in a nationwide reconnaissance. In our study, antibiotics and associated degradation products were found in water samples collected at only two streams below effluent discharges, Mud Creek and Spring Creek (Table 4). During March and April 2004, only 4 of 45 antibiotics and associated degradation products measured were found in detectable amounts. At Spring Creek (Site 12), two antibiotics in the macrolides group were found, including trimethoprim and anhydro-erythromycin, a degradation product of the parent antibiotic erythromycin. At Mud Creek (Site 9), these same two macrolides plus two additional antibiotics were found, including ofloxacin from the quinolones group and sulfamethoxazole from the sulfonamides group. These three antibiotics and one antibiotic degradation product persisted in the water column and were observed at the site (Site 10) further downstream from the effluent discharge at Mud Creek, where the concentrations of anhydro-erythromycin, trimethoprim, and sulfamethoxazole decreased downstream likely due to dilution and in-stream processes.

In August 2004, 8 of 45 antibiotics and associated degradation products were found in measurable concen-

Table 4. Summary of analytical results for several antibiotics in the water samples collected from selected streams in north-central and northwestern Arkansas, March, April, and August 2004.

Antibiotic	RL†	Frequency‡	Reported concentration in water samples		
			Minimum	Median	Maximum
	μg L^{-1}	%	μg L^{-1}		
Beta lactams					
Amoxicillin	0.20, 0.01	0	–	–	–
Ampicillin	0.10, 0.01	0	–	–	–
Cefotaxine	0.10, 0.01	0	–	–	–
Cloxacillin	0.10, 0.01	0	–	–	–
Oxacillin	0.10, 0.01	0	–	–	–
Penicillin G	0.10, 0.01	0	–	–	–
Penicillin V	0.10, 0.01	0	–	–	–
Macrolides					
Erythromycin§	0.10, 0.005	10	0.154	–	0.175
Anhydro-erythromycin§	0.05, 0.005	24	0.050	0.200	1.209
Lincomycin	0.05, 0.005	0	–	–	–
Ormetoprim	0.05, 0.005	0	–	–	–
Roxithromycin	0.10, 0.005	0	–	–	–
Trimethoprim§	0.05, 0.005	24	0.008	0.058	0.19
Tylosin§	0.10, 0.005	10	0.008	–	0.012
Virginiamycin	0.10, 0.005	0	–	–	–
Quinolones					
Ciprofloxacin§	0.05, 0.005	10	0.027	–	0.039
Clinafloxacin	0.05, 0.005	0	–	–	–
Flumequine	0.05, 0.005	0	–	–	–
Lomefloxacin	0.05, 0.005	0	–	–	–
Norfloxacin	0.05, 0.005	0	–	–	–
Ofloxacin§	0.05, 0.005	19	0.094	0.100	0.109
Oxolinic acid	0.05, 0.005	0	–	–	–
Sarfloxacin	0.05, 0.005	0	–	–	–
Sulfonamides					
Sulfachloropyridazine	0.05, 0.005	0	–	–	–
Sulfadiazine	0.05, 0.005	0	–	–	–
Sulfadimethoxine§	0.05, 0.005	10	E 0.003¶	–	E 0.004
Sulfamerazine	0.05, 0.005	0	–	–	–
Sulfamethazine	0.05, 0.005	0	–	–	–
Sulfamethoxazole§	0.05, 0.005	19	0.196	0.361	0.5
Sulfathiazole	0.05, 0.005	0	–	–	–
Tetracyclines					
Chlorotetracycline	0.10, 0.01	0	–	–	–
Anhydro-chlorotetracycline	0.10, 0.01	0	–	–	–
Epi-anhydro-chlorotetracycline	0.10, –	0	–	–	–
Epi-chlorotetracycline	0.10, –	0	–	–	–
Iso-chlorotetracycline	0.10, –	0	–	–	–
Iso-epi-chlorotetracyline	0.10, –	0	–	–	–
Demeclocycline	0.10, 0.01	0	–	–	–
Doxycycline	0.10, 0.01	0	–	–	–
Minocycline	0.10, 0.01	0	–	–	–
Oxytetracycline	0.10, 0.01	0	–	–	–
Epi-oxytetracycline	0.10, –	0	–	–	–
Tetracycline	0.10, 0.01	0	–	–	–
Anhydro-tetracycline	0.20, 0.01	0	–	–	–
Epi-anhydro-tetracycline	0.10, –	0	–	–	–
Epi-tetracycline	0.10, –	0	–	–	–

† Method reporting limiting from the U.S. Geological Survey Organic Chemistry Research Laboratory. The first value is the RL for samples collected in March and April 2004; the second value is the RL for samples collected from Mud Creek in August 2004.
‡ Frequency of constituent detection in percent for 21 water samples collected in March, April, and August 2004.
§ Detected in measurable concentrations by analytical methods used in this study.
¶ The term "E" defines concentrations that were estimated at or below the reporting limit of the method used.

trations at Mud Creek. Thus, the number of detections at Mud Creek downstream from the effluent discharge doubled (Table 1 and 4). The same four antibiotics were detected in the second set of samples plus four additional antibiotics, including erythromycin and tylosin from the macrolides, ciprofloxacin from the quinolones, and sulfadimethoxine from the sulfonamides (Table 4). As observed in March 2004, these seven antibiotics and one associated degradation product persisted in the water column and were observed further downstream at Mud Creek (Site 10). Concentrations of the two sulfonamides increased at the site (Site 10) further downstream in August 2004, whereas concentrations of the other chemicals decreased. The number of detections likely increased because the method reporting limits were an order of magnitude less for water samples collected and analyzed in August 2004 than in March and April.

Many of the antibiotics and associated degradation products measured were not detected in water samples collected from any of sites at the selected streams in our study (Table 4). This is not surprising given the nature of the chemical structure and functional groups, and the

affinity of many of these compounds to adsorb to soils and benthic sediments (Tolls, 2001; Thiele-Bruhn, 2003). Several studies have shown that antibiotics and associated degradation products accumulate in aquatic sediments and have found that the concentrations of these chemicals were often 20 to 1000 times greater in sediments than the overlying water column (e.g., see Capone et al., 1996; Ingerslev et al., 2001). It is likely that benthic sediments provide a time-integrated sample of antibiotics and associated degradation products released into effluent dominated streams, and we should consider collecting benthic sediments and extracting these chemicals during future monitoring, especially at Mud Creek and Spring Creek.

The introduction of antibiotics and other antimicrobial agents (e.g., triclosan) into the environment, particularly aquatic systems, is an emerging concern. The presence of these chemicals may alter algal growth and community structure (Andreozzi et al., 2004; White et al., 2005; Wilson et al., 2003), potentially impacting ecological integrity and ecosystem function through changing community structure at the most basic level (i.e., algal taxonomy). Several studies have also shown that antibiotic resistance has been acquired in multiple bacterial lineages in the clinical environment and also aquaculture facilities (e.g., Guardabassi et al., 2000; Petersen et al., 2002). However, typical antibiotic concentrations found in aquaculture are much greater than that observed in flowing streams, including those sampled in this study. Little is known about the potential ecological and human health implications related to the occurrence of these antibiotics and chronic environmental exposure at relatively low concentrations in effluent dominated streams, such as those in our study.

CONCLUSIONS

Overall, many different pharmaceuticals and other chemicals (42 out of 108 targeted chemicals) were detected in the collected water samples at the selected streams in northwestern and north-central Arkansas, and these different chemicals comprised many different mixtures at the various water-quality monitoring sites. Many concentrations were relatively low (<1 μg L^{-1}) and often these values were estimated because concentrations were less than the reporting limits. However, some concentrations were greater than 1 μg L^{-1}, including three steroids, three detergent metabolites, a widely used fragrance and an antibiotic degradation product. It was apparent that municipal WWTP effluent discharges significantly increased the number of chemicals detected and the total measured concentration; four chemical categories were generally responsible for these increases, including detergent metabolites, fire retardants, fragrances and flavors, and steroids. Also, antibiotics were only found in water samples collected downstream from municipal effluent discharges. Once studies identify the mixtures of organic chemicals prevalent in selected streams, further investigations need to move beyond simple occurrence studies to evaluate the fate and transport of these chemicals and provide a better understanding of the potential impacts of these chemicals on aquatic biota.

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